CLAIMS

1. A microporous hollow support fiber membrane comprising solvent-resistant polybenzimidazole having the following characteristics:

(i) surface pores less than one micron in diameter;
(ii) nitrogen permeance of at least 5 $m^3/m^2 \bullet hr \bullet atm$;
(iii) tensile strength of at least 100 g/fil;
(iv) elongation at break of at least 10%;
(v) an inner diameter of from about 200 to about 1000 microns; and
(vi) a wall thickness of from about 30 to about 200 microns.

2. The support fiber membrane of claim 1 having a nitrogen permeance of at least 10 $m^3/m^2 \bullet hr \bullet atm$, a tensile strength of at least 200 g/fil and an elongation at break of at least 15%.

3. A separation module comprising:

(a) a chamber having feed and retentate ends and means for removing permeate near the feed end;
(b) a bundle of thin film composite hollow fiber membranes arranged substantially parallel to each other in said chamber, each of said composite hollow fiber membranes comprising a microporous solvent-resistant hollow support fiber comprising polybenzimidazole having at least one permselective coating on the surface of said support fiber, said support fiber having the following characteristics:

(i) surface pores less than one micron in diameter,

(ii) nitrogen permeance of at least 5 $m^3/m^2 \cdot hr \cdot atm$,

(iii) tensile strength of at least 100 g/fil,

(iv) elongation at break of at least 10%,

(v) an inner diameter of from about 200 to about 1000 microns, and

(vi) a wall thickness of from about 30 to about 200 microns; and

(c) means for securing and sealing said bundle of hollow fiber membranes to said chamber at said feed and retentate ends so as to permit fluid communication with a feed stream.

4. The module of claim 3 wherein said support fiber has a nitrogen permeance of at least 10 $m^3/m^2 \cdot hr \cdot atm$, a tensile strength of at least 200 g/fil and an elongation at break of at least 15%.

5. A method of making a polybenzimidazole microporous hollow fiber membrane comprising the steps:

(a) providing a polymer solution comprising 15 to 30 wt% polybenzimidazole, 2 to 5 wt% high molecular weight pore-former having a molecular weight of ≥1000 daltons, 5 to 30 wt% low molecular weight pore-former having a molecular weight of ≤100 daltons, and a solvent;

(b) forming a spun membrane by extruding said polymer solution of step (a) through an orifice at a temperature of 25° to 60°C while simultaneously injecting a coagulating fluid through a needle located in said orifice;

(c) providing a quench bath;

(d) passing the spun membrane of step (b) through said quench bath at a temperature of from 10° to 40°C to form a microporous hollow fiber membrane; and

(e) rinsing said membrane of step (d).

6. The method of claim 5 wherein said high molecular weight pore-former is selected from the group consisting of polyvinyl pyrollidinone, polyvinyl alcohol, polyvinyl acetate, polyethylene glycol and polypropylene glycol; and said low molecular weight pore-former is selected from the group consisting of (i) a lower alkanol, (ii) a polyfunctional alcohol, (iii) ester and ether derivatives of an alkanol, (iv) ester and ether derivatives of a polyfunctional alcohol, (v) mixtures of (i)-(iv), and (vi) mixtures of water and at least one of (i)-(v).

7. The method of claim 5 wherein said high molecular weight pore-former is polyvinyl pyrollidinone and said low molecular weight pore-former is n-propanol.

8. The method of claim 5, including the following additional steps:

(f) drying said membrane of step (d); and

(g) post-treating said membrane of step (f).

9. The method of claim 8 wherein step (g) is selected from annealing and crosslinking.

10. The method of claim 9 wherein step (g) is crosslinking and said crosslinking is conducted by contacting said membrane with a crosslinking solution comprising a multi-functional alkyl halide in a solvent followed by heating said membrane sufficiently to cause crosslinking to take place.

11. The method of claim 10 wherein said solvent is selected from a ketone and an ether and said multi-functional alkyl halide has a structure selected from

$$X\text{-}(CH_2)_n\text{-}CH_2\text{-}X \quad \text{and}$$

$$X\text{-}(CH_2)_a\text{-}\underset{\underset{\displaystyle CH_3}{|}}{\underset{\displaystyle (CH_2)_c}{\underset{|}{CH}}}\text{-}(CH_2)_b\text{-}X$$

where X is selected from Br and Cl,

n is an integer of from 1 to 11,

a is an integer of from 1 to 10,

b is a number of from 0 to 4, and

c is a number of from 0 to 6.

12. The method of claim 11 wherein said multi-functional alkyl halide is dibromobutane, said solvent is selected from the group consisting of acetone, methyl isobutyl ketone, methyl ethyl ketone and pentanone, and said heating is conducted at a temperature of from 25° to 200°C for 0.5 to 48 hours.

13. The method of claim 10 wherein a surface of said hollow fiber membrane is coated with at least one permselective coating.

14. The method of claim 13 wherein said at least one permselective coating is coated on the lumens of said hollow fiber membrane.

15. The method of claim 13 wherein said at least one permselective coating is a crosslinked polymer selected from the group consisting of poly (acrylic acids), poly (acrylates), polyacetylenes, poly (vinyl acetates), polyacrylonitriles, polyamines, polyamides, polyethers, polyurethanes, polyvinyl alcohols,

polyesters, cellulose, cellulose esters, cellulose ethers, chitosan, chitin, polymers containing hydrophilic groups, elastomeric polymers, halogenated polymers, fluoroelastomers, polyvinyl halides, polyphosphazenes, poly (trimethylsilylpropyne), polysiloxanes, poly (dimethyl siloxanes) and copolymers and blends thereof.

16. The product of the method of any of claims 5 or 9-15.

17. A method of crosslinking a polybenzimidazole membrane comprising the following steps:

(a) providing a crosslinking solution comprising a multi-functional alkyl halide in a solvent;

(b) soaking said membrane in said crosslinking solution from 0.5 to 48 hours and at a temperature from 25° to 150°C; and

(c) heating said membrane fro 0.5 to 48 hours at a temperature of 25° to 200°C.

18. The method of claim 17 wherein said membrane has a morphology selected from the group consisting of hollow fiber, tubular and flat.

19. The method of claim 17 wherein said membrane has a porosity selected from the group consisting of microporous, nonporous, isoporous and asymmetric.

20. The method of claim 18 wherein said membrane has a porosity selected from the group consisting of microporous, nonporous, isoporous and asymmetric.

21. The product of the method of any of claims 17-20.